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(54)Method of removing mold from plastic bottles and mold removing additive

(57)Mold removal from plastic bottles such as polyester and polycarbonate bottles is significantly enhanced by adding to a typical caustic soaking solution an effective amount of a complex polyphosphate such as sodium tripolyphosphate and a surfactant. The combination of the phosphate and the surfactant significantly enhances mold removal. Mold removal can be further enhanced by combining with the phosphate and surfactant either a phosphonate and/or a chelating agent such as sodium glucoheptonate. This combination signficantly improves mold removal, but does not increase stress cracking of the plastic bottle.

Description

Background of the Invention

In many countries, bottles such as soft drink bottles are repeatedly cleaned and reused. The used bottles are passed through a bottle-washing apparatus which cleans the bottle, permitting it to be refilled and reused. Both plastic and glass bottles are subject to reuse.

Due to the physical characteristics of glass versus plastic bottles, the two are treated somewhat differently. Glass bottles are subjected to a highly alkaline wash containing 2-4% sodium hydroxide at a temperature of generally 70°C or higher. This is quite effective in removing most soils.

One soil which is particularly difficult to remove is mold. Mold tightly adheres to the surface of bottles, both plastic and glass, and is relatively difficult to remove. Mold can be removed from glass bottles by simply operating at temperatures above 60°C, which is typically done. But with plastic containers, this is not possible. At temperatures higher than 60°C, most plastic containers will shrink. Further, higher temperatures and higher alkalinity promote stress cracking which is unsightly and eventually can cause the bottle to leak or break open. Certain surfactants also promote stress cracking. Other harsh chemicals such as bleaches will remove mold. But these would corrode the equipment and therefore are unacceptable. EDTA is currently used to enhance mold removal. However, this is not always totally effective.

Compounding the problem of mold removal is the fact that its mechanism of attachment to a surface is not completely understood. It is believed that a protein and/or a glycoprotein is involved in the attachment, but the exact chemical nature of this attachment, as well as the physical nature of this attachment, are not completely understood.

Summary of the Invention

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It is an object of the present invention to provide an additive for a bottle-washing apparatus which effectively removes mold from the surface of plastic articles such as bottles without destroying the plastic article.

More particularly, the present invention is premised upon the realization that an alkaline wash solution which includes an effective amount of a complex phosphate, in combination with a suitable surfactant, either nonionic or anionic, will effectively remove mold from plastic surfaces at temperatures less than 60°C. This, in turn, permits the removal of mold from the plastic surface without destruction of the plastic container.

More particularly, the present invention is premised on the realization that the removal of mold is enhanced by the further addition of an effective amount of a phosphonate which is also useful in the cleaning of the bottle. In a preferred embodiment, the bottle-washing solution will also include a chelating agent such as sodium gluconate, sodium gluconate, or sodium boroheptonate. Although gluconates are considered to be less effective at milder alkalinities, it provides a significant improvement in mold removal in this system. These combined components provide an extremely effective bottle-washing solution which outperforms currently-used bottle washing formulations in the removal of mold from plastic surfaces. Further, the formulation of the present invention, even with the added surfactant, does not further promote stress cracking relative to commercially available formulations. Although formulated primarily for plastic containers, this formulation will also assist in removal of mold from glass containers as well.

The objects and advantages of the present invention will be further appreciated in light of the following detailed description and drawing description in which:

Brief Description of Drawing

The Figure is a graph showing the test results of Example 2 demonstrating mold removal from bottles in a commercial bottle washing apparatus.

Detailed Description

The present invention is a method and solution for cleaning reusable plastic bottles and is particularly directed at mold removal. The reusable plastic bottles cleaned according to the present invention can be formed from many different plastics. Most reusable plastic bottles are currently formed from polyesters such as polyethylene terephthalate, polybutylene terephthalate, and polycarbonate. Basically any reusable plastic bottle which can be subjected to an alkaline wash is suitable for use in the present invention.

By way of background, bottle washing apparatuses generally include three or four sections. The bottles are introduced into the machine and supported throughout the washing process by individual holders or pockets. Bottles are initially directed to a prerinse section which is designed to remove large particles and labels. In this section water and residuals from the cleaning process are directed at the bottles as they are introduced into the machine.

Next, the bottles are conveyed to a cleaning or soaking section where they are soaked in a caustic solution at an

elevated temperature, generally no higher than 60°C for plastic bottles such as PET bottles. After 7 to about 30 minutes (generally 9-11 minutes) in the soaking section the bottles are taken to a warm rinse and then to a final potable water rinse. The final rinse is then reused for the subsequent initial prerinse.

The cleaning or soaking solution is a caustic solution. Generally this contains 0.5 to 5.0%, and preferably 1.0 to 3.0%, sodium hydroxide for PET containers. This acts to clean the bottles and dissolve metals such as metal foils of the label and the closure rings. This caustic solution also, in combination with temperature and contact time, renders the bottles commercially sterile. However, at caustic concentrations greater than 3% stress cracking of the plastic bottles is excessive.

In addition to the caustic, the soaking solution will include an additive to enhance mold removal. The mold-removing additive is a combination of complex phosphates, surfactants, and preferably chelating agents, particularly gluconates and related agents, as well as threshold water conditioners such as the phosphonates. The additive itself is formed in a concentrated stable aqueous solution or a premixed powder which is formulated with the above components in a proportion to provide for effective use concentration of all the components when added.

Generally the soaking solution in the bottle washing apparatus, i.e., at use concentration, should have 1000 to 2500 ppm of the complex phosphates. Complex phosphates include the common polyphosphates. Particular phosphates which can be employed include sodium tripolyphosphate, potassium tripolyphosphate, sodium potassium tripolyphosphate, tetrapotassium pyrophosphate, and tetrasodium pyrophosphate, as well as others.

In addition to the complex phosphate, the wash solution must include an effective amount of a surfactant, either an anionic surfactant, a nonionic surfactant, an amphoteric surfactant, or a mixture thereof. It is important that the surfactants be selected so that they do not promote stress cracking of the plastic bottles. The most effective nonionic surfactants are the polyalkoxylated fatty alcohols and the polyethoxylated straight chain alcohols. These are also preferred since they contribute to foam control.

Commercially available alkoxylated alcohol surfactants include Makon NF 12, Plurafac LF 221, Plurafac LF 223, Plurafac LF 431, Polytergent SLF18, and Triton DF12, a modified polyethoxylated alcohol. Other suitable nonionics include alkyl polyglycosides such as Triton BG10, Triton CGIO, and EO -PO block copolymers such as Industrol N-3.

Suitable anionics include sodium C₁₄ - C₁₆ alpha olefin sulfonates such as Bioterge AS-40, alkyl aryl sulfonates, carboxylated alcohols such as Polytergent CSI, alkali metal salts of phosphate esters such as Triton H66, alkali metal alkanoates such as Monatrope 1250, fatty alcohol polyglycol ether carboxylic acids such as Akypo LF 4, dioctylsulfosuccinate such as Monawet MO70, modified ethoxylates such as Mona NF 10 and Triton DF 20, and alkali metal xylene sulfonates such as Eltesol PX93.

Suitable amphoterics include alkyl and alkyl alkoxy iminodiproprionates such as lauryl iminodiproprionate and isodecyloxypropyl iminodipropionate sold under the trademark Alkali surfactant.

Generally 200=1000 ppm surfactant will be used in the soaking solution. The upper limit is determined by economics. Concentrations greater than 1000 ppm provide little added benefit. A blend of surfactants may be preferred to reduce stress cracking and improve efficiency.

In addition to the phosphate and surfactant, the formulation optionally includes 500-1000 ppm of an organic phosphonate. Typically used organophosphonates include aminotrimethylene phosphonic acid, 1-hydroxyethylene (1,1 diphosphonic acid), hexamethylenediaminetetramethylene phosphonic acid, diethylenetriaminepentamethylene phosphonic acid, and phosphonobutanetricarboxylic acid. These assist not only in mold removal, but also carry over to the rinse section of the bottle washer to provide threshold water conditioning in that section, reducing scale.

Finally, the present invention can also include one or more chelating agents. Suitable chelating agents are the gluconates and comparable compositions. Particular chelating agents include sodium gluconate or gluconic acid, sodium glucoheptonate, and sodium boroheptonate. These should be present in the wash solution at a concentration of from 500 ppm to 2000 ppm.

The concentrated formulation can be stated in terms of a ratio of parts by weight actives. The mold removing composition of the present invention will generally include from 10 to 25 parts by weight of the complex phosphate, 2 to 10 parts by weight of the surfactant, and optionally but preferably 5 to 10 parts by weight of the phosphonate, and 5 to 20 parts by weight of the chelating agent, which is preferably sodium gluconate. Said surfactant is desirably either an anionic surfactant selected from alkylaryl sulfonates, C₁₄-C₁₆ alpha olefin sulfonates and alkyl sulfosuccinates, or a nonionic surfactant selected from polyalkoxylated fatty alcohols and polyethoxylated straight chain alcohols. Most preferred surfactant for use in said composition is iminodipropionate. If said composition is formulated as a liquid, it will also include an amount of caustic liquid to maintain an alkaline pH. The balance of the product would then be water. Generally, it is desirable to have as high an actives content as possible. With the present formulation, an actives content of 40% to 50% can be achieved.

Table 1 shows three different liquid formulations of the present invention. With liquid formulations, each of the individual components is simply combined with water. The order of addition is not significant. These are blended until a stable solution is formed.

Table 1

| Raw Materials | Formula 1 | Formula 2 | Formula 3 |
|-------------------------------|------------|------------|-------------|
| Soft Water | 50.87 | 51.07 | 53.24 |
| Sodium Gluconate | 7.0 | 7.0 | 7.0 |
| Dequest 2000 | 3.0 | 3.0 | 3.0 |
| Caustic Liquid 50% | 2.0 | 2.0 | 2.0 |
| KTPP Liquid 50 | 27.13 | 27.13 | 27.13 |
| Plurafac LF221 (Nonionic 95%) | | 1.0 (0.95) | 0.32 (0.30) |
| Plurafac LF223 (Nonionic 98%) | 1.0 (0.98) | | 0.31 (0.30) |
| Triton BG 10 (Nonionic 70%) | | | |
| Akypo LF4 (Anionic 90%) | 2.0 (1.8) | 2.0 (1.8) | 2.0 (1.8) |
| Eltesol PX93 | 7.0 | 6.8 | 5.0 |

An amount of the concentrated composition is added to the soaking solution to provide an acceptable level of actives in the soaking solution. Generally, the use concentration will be 0.5 to 1.5% with 1.25% preferred.

The present invention is illustrated by way of the following non-limiting examples showing preferred methods of practicing the invention.

EXAMPLE 1

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In order to test the bottle washing composition of the present invention, and to compare this with commercially-available additives, actual consumer bottles containing mold colonies were collected. Approximately 50% of the moldy bottles had greater than 10 mold colonies. These were then passed through a bottle washing apparatus under identical conditions with different standard soaking solutions and mold removal results were compared. Initially, 2.8% sodium hydroxide was used by itself. This cleaned 36% of the bottles, but left 26% of the bottles with greater than 10 mold colonies. Two commercially available products were tested, each with 2.8% NaOH and a commercially available additive. These cleaned 46% and 54% of the bottles, respectively, both leaving 24% with greater than 10 mold colonies. 0.25% w/v sodium tripolyphosphate (1720 ppm) was then added to the solution containing the commercially available product. This, in turn, cleaned 56% of the bottles and left 12% with greater than 10 mold colonies. To this solution was then added 0.02% w/v surfactant (200 ppm alkoxylated alcohol). With this combined solution of sodium hydroxide, sodium tripolyphosphate and surfactant, 60% of the bottles were cleaned leaving only 6% of the bottles with greater than 10 mold colonies.

EXAMPLE 2

In a second study, consumer bottles containing mold colonies were collected and separated into 7 groups. The Figure is a graph depicting the seven groups. The first group was not washed and contained 23% bottles with greater than 10 mold colonies (negative control). A second group was sent through a bottle washing solution with 2.8% sodium hydroxide (standard control). This cleaned 42% of the bottles and left 23% with greater than 10 mold colonies. Two commercially available products listed at RPB and MR were again tested with 2.8% NaOH. These cleaned 51% and 46% of the bottles, respectively, leaving greater than 10 mold colonies in 27% and 18%, respectively. Formula 3, listed as "X" in the Figure, was then added to the sodium hydroxide at 0.4% concentration. This resulted in 46% of the bottles being cleaned with 17% of the bottles left with greater than 10 mold colonies. The concentration was then increased to 0.8%, resulting in 51% of the bottles being cleaned and 21% containing more than 10 mold colonies. Finally, at 1.25% concentration, 65% of the bottles were cleaned, with 13% of the bottles having more than 10 mold counts.

These tests were all relatively severe and they were not expected to achieve 100% cleaning or 100% mold removal. The results shown by Formula 3 were considered significantly better than commercially available products, particularly at the 1.25% concentration level.

These test results indicate that the sodium tripolyphosphate, in combination with the nonionic surfactant, is particularly effective at removing mold, and that the Formula 3 is a significant improvement over the combination of sodium tripolyphosphate and nonionic surfactant by itself. Further, test results indicated that the addition of Formula 3, in spite

of the use of the surfactant, promoted less stress cracking than other commercial additives. Thus, the present invention provides better mold removal and promotes less stress cracking than commercially available products.

Exemplary dry formulations which are useful in assisting mold removal are listed below, as well as an indication of mold removal efficacy in laboratory studies:

| POWDERS | | | | | | |
|---------------------|----------------|-------|--|--|--|--|
| Material: | Weight Percent | | | | | |
| STPP, granular | | 45.00 | | | | |
| SKTP, granular | 63.00 | | | | | |
| Sodium gluconate | 25.00 | 25.00 | | | | |
| Dequest 2016D | 6.00 | 6.00 | | | | |
| Makon NF 12 | 6.00 | | | | | |
| Soda Ash | | 15.00 | | | | |
| Poly Tergent SLF-18 | | 6.00 | | | | |
| Poly Tergent CS-1 | | 3.00 | | | | |
| | | | | | | |
| Mold Removal | 90-100% | 100% | | | | |
| W/w additives | 0.4% | 0.4% | | | | |
| NaOH | 2.80% | 1.50% | | | | |

Other exemplary liquid formulations are listed below.

| | | LIQUIE | os | | | | | |
|---------------------------------------|----------------|--------|-------|-------|-------|-------|-------|-------|
| Material: | Weight Percent | | | | | | | |
| Water, soft | 74.75 | 74.50 | 68.50 | 49.75 | 68.10 | 70.30 | 70.50 | 69.20 |
| KTPP, 60% solution | 24.00 | 24.00 | 30.00 | 40.00 | | | | |
| Sodium gluconate | | | | | 7.00 | 7.00 | 7.0 | 5.0 |
| Triton DF12 | | 0.25 | 0.25 | | | | | |
| Triton DF 16 | 0.25 | | | | 1. | | | |
| Alkali Surfactant | 1.00 | 1.25 | 1.25 | | | | | |
| Sodium Xylene Sulfonate, 40% solution | | | | 10.00 | | | | |
| Mona NF 10 | | | | 0.25 | | | | |
| Inustrol N-3 | | | | | 1.50 | | | |
| NaOH, 50% liquor | | | | | 2.00 | 2.00 | 2.0 | 4.0 |
| Dequest 2000 | | | | | 3.00 | 3.00 | 3.0 | 3.30 |
| SKTP, granular | | | | | 12.00 | 12.00 | 12.00 | 12.50 |
| PolyTergent SLF-18 | | | | | | 1.40 | 2.00 | 1.00 |
| PolyTergent CS-1 | | | | | 3.00 | 2.00 | | 3.00 |
| Makon NF-12 | | | | | | ri e | 5 - 1 | |

(continued)

| | | LIQUI | DS | | | | | |
|---------------------------|----------------|-------|------|--------|------|-------|------|------------|
| Material: | Weight Percent | | | | | | | |
| Monatrope 1250 | | | | | | | | |
| Alkenyl Carboxy Sulfonate | | | | | 3.40 | 2.30 | 3.50 | 2.00 |
| | | | | | | | | |
| Use at % v/v | 1.70 | 1.70 | 1.40 | 1.00 | 0.40 | 1.00- | 0.40 | 1.50 |
| % mold removal | | | | 90-100 | 100 | 100 | 100 | 90- 100 |
| % NaOH | | | | 2.80 | 1.5 | | 1.50 | 1.50 |

Each of these significatly enhance mold removal in an alkaline bottle washing solution.

Claims

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- 20 1. A method of removing mold colonies from plastic bottles comprising treating said bottles with a solution, said solution containing a concentration of caustic effective to clean said bottles, in combination with an amount of a complex phosphate and surfactant, said amount being effective to achieve enhanced mold removal at a temperature less than 60°C without promoting stress cracking.
- 25 2. The method claimed in claim 1, wherein said complex phosphate is selected from the group consisting of sodium tripolyphosphate, potassium tripolyphosphate, sodium potassium tripolyphosphate, tetrapotassium pyrophosphate, and tetrasodium pyrophosphate.
- 3. The method claimed in claim 2, wherein said solution comprises from 1000 to 2500 ppm of said complex phosphates.
 - 4. The method claimed in claim 1, wherein the solution comprises from 200 ppm to 1000 ppm of said surfactant.
- 5. The method claimed in claim 4, wherein said surfactant is selected from the group consisting of polyalkoxylated fatty alcohols, polyethoxylated straight chain alcohols, alkyl aryl sulfonates, C14-C16 alpha olefin sulfonates, and sodium dioctylsulfosuccinate.
 - 6. The method claimed in claim 1, wherein said solution further comprises from 500 to 1000 ppm of an organic phosphonate.
 - 7. The method claimed in claim 6, wherein said organic phosphonate is selected from the group consisting of amino trimethylene phosphonic acid, 1-hydroxyethylene(1,1 diphosphonic acid), hexamethylenediaminetetramethylene phosphonic acid, diethylenetriaminepentamethylene phosphonic acid, and phosphonobutanetricarboxylic acid.
- 8. The method claimed in claim 1, wherein said solution further includes a chelating agent selected from the group consisting of sodium gluconate, sodium glucoheptonate, and sodium boroheptonate.
 - 9. The method claimed in claim 8, wherein said chelating agent is present in an amount from 500 to 2000 ppm.
- 10. A method of removing mold from plastic bottles comprising soaking said bottles in a caustic solution at a temperature less than 60°C, wherein said solution includes from:

1000 to 2500 ppm complex phosphate;

200 to 1000 ppm surfactant selected from the group consisting of nonionic and anionic surfactants;

500 to 1000 ppm organic phosphonate;

500 to 2000 ppm of a chelating agent selected from a group consisting of sodium gluconate, sodium glucoheptonate, and sodium boroheptonate.

11. A mold removal agent for use with an alkali solution comprising:

10 to 25 parts by weight of a complex phosphate;

2 to 10 parts by weight of a surfactant;

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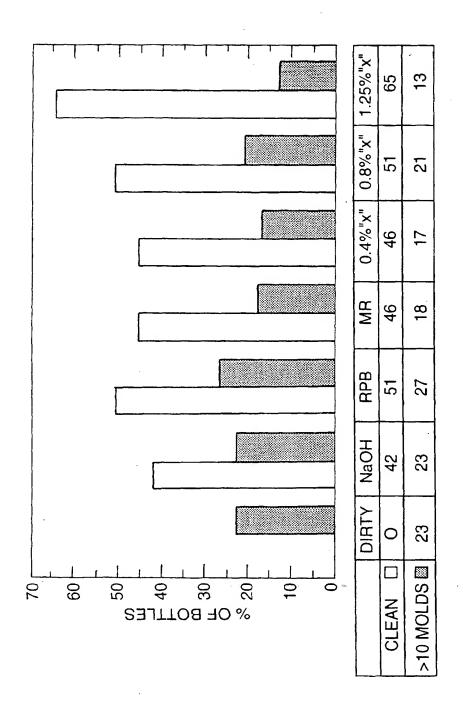
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- 5 to 10 parts by weight of an organic phosphonate;
- 5 to 20 parts by weight of a chelating agent selected from the group consisting of gluconates, glucoheptonates, or boroheptonates, said parts by weight provided on an actives basis, the balance being water.
- 12. The agent claimed in claim 11 wherein said organic phosphonate is selected from the group consisting of amino trimethylene phosphonic acid and 1-hydroxyethylene (1,1 diphosphonic acid), hexamethylenediaminetetramethylene phosphonic acid, diethylenetriaminepentamethylene phosphonic acid, and phosphonobutanetricarboxylic acid.
- 13. The agent claimed in claim 11 wherein said chelant is sodium gluconate.
- 14. The agent claimed in claim 11 wherein said surfactant is selected from the group consisting of alkylaryl sulfonates, $C_{14\cdot16}$ alpha olefin sulfonates, and alkyl sulfosuccinates.
- 15. The agent claimed in claim 11 wherein said surfactant is a nonionic surfactant selected from the group consisting of polyalkoxylated fatty alcohols and polyethoxylated straight chain alcohols.
 - 16. The agent claimed in claim 11 wherein said surfactant is an iminodipropionate.

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(71) Applicants:

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(54)Method of removing mold from plastic bottles and mold removing additive

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EUROPEAN SEARCH REPORT

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| Category | | ndication, where appropriate, | Relevant | CLASSIFICATION OF TH | |
|----------|---|----------------------------------|---|---------------------------------------|----|
| | of relevant pass | ages | to claim | APPLICATION (Int.Cl.6) | |
| Α | DATABASE WPI | | 1,2,5,11 | C11D3/06 | |
| | Section Ch, Week 86 | | | C11D3/36 | |
| | Derwent Publication | | | | |
| | Class A97, AN 86-18 XP002005616 | 0120 | | | |
| İ | | EOS KK), 5 June 1986 | | | |
| | * abstract * | . , | | | |
| . | | | | | |
| Α | DATABASE WPI | 10 | 1,2,8, | | |
| | Section Ch, Week 95 Derwent Publication | | 11-14 | | |
| | Class D25, AN 95-07 | | | | |
| | XP002037099 | | | | |
| | & JP 06 346099 A (T | EEPOL KK) | | | |
| | , 20 December 1994 | | | | |
| | * abstract * | | | | |
| Α | US 3 669 893 A (CLA | RKE FREDRIC B ET AL) | 1,2,8, | | |
| | 13 June 1972 | | 11-14 | | |
| | * claims; examples | * | | TEOLISION SISTER | |
| | | | | TECHNICAL FIELDS SEARCHED (Int.CI. | 6) |
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| С | ATEGORY OF CITED DOCUMENTS | | ciple underlying the i document, but publi | | |
| | icularly relevant if taken alone icularly relevant if combined with anot | after the filing | | one on o | |
| doc | ament of the same category | £ : document cité | d for other reasons | , | |
| | inological background -written disclosure | | e same patent family | | |

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 97 20 3528

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

07-01-1999

| | Patent document ed in search repo | | Publication date | | Patent family member(s) | Publication date |
|----|--------------------------------------|---|-------------------------------|----------------|------------------------------------|-------------------------------------|
| US | 3669893 | A | 13-06-1972 | BE DE FR | 736406 A 1937031 A 2017949 A | 22-01-197 22-01-197 29-05-197 |
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